NANO REVIEW

Gold nanowires and the effect of impurities

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Abstract Metal nanowires and in particular gold nanowires have received a great deal of attention in the past few years. Experiments on gold nanowires have prompted theory and simulation to help answer questions posed by these studies. Here we present results of computer simulations for the formation, evolution and breaking of very thin Au nanowires. We also discuss the influence of contaminants, such as atoms and small molecules, and their effect on the structural and mechanical properties of these nanowires.

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Introduction

Modern experimental techniques such as Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM) and High Resolution Transmission Electron Microscopy (HRTEM) that allow visualization and, more importantly, manipulation of individual atoms, made possible nanoscience. Along with these new possibilities new challenges were presented to science, and one way to complement the understanding of these new questions is the use of computer simulations, such as molecular dynamics, that in the last few

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years have also evolved a great deal due to the computer capability of present computers as well as the improvement of algorithms. These new simulation methods, implemented at levels ranging from effective potentials to tight binding based, up to ab initio electronic structure, have helped to aid the understanding of experiments as well as stimulate new experiments, since these techniques now have predictive power. The research in basic and applied science which is associated with the development of devices at nanoscale makes the study of nanowires and nanocontacts of paramount importance. The reason is that nanosized devices require nanosize contacts. The interesting fact is that at this size scale, the behavior of nanowires is different than the metal in bulk form. Atomic size metal nanowires exhibit, for example, quantized conductance and increase in reactivity and strength, among other interesting properties.

Atomic size wires can be produced via a variety of techniques, e.g., if a metallic tip is retracted from a metallic surface [1]. Suspended monoatomic nanowires have been detected with the use of controllable breaking junctions [2], atomic force microscopy [3] and are imaged with high resolution transmission electron microscopy [4]. Using this HRTEM technique, real time evolution of nanowires can be observed. For these reasons theoretical studies of such systems have been intense.

Metallic nanowires were in fact predicted by simulations. Mostly using molecular dynamics with classical many body potentials, simulations have predicted new structures [5, 6]. An interesting example of a proposal of new structures is the work of Gulseren, Ercolessi and Tosatti [6] that have predicted, based in computer simulations for classical potentials, that Al and Pb thin

wires would prefer to have what they called weird structures as opposed to the expected crystalline multifaceted structures.

The research in computer simulations for metallic nanowires is been pursued using a variety of techniques, and the present work focus on the use of two ones based on Density Functional Theory (DFT) [7, 8]. Tight binding molecular dynamics (TBMD) is used for the dynamical evolution of the NWs and DFT electronic structure methods, using either localized (SIESTA code) or plane waves (VASP code) basis set, are used to study the final stages of evolution of these wires, as well as the effect of contamination with light impurities.

Methods

The tight-binding molecular dynamics method explicitly includes the electronic structure, but is much faster than first principles methods. Of course, this gain in speed comes with the cost of loosing some of the flexibility of fully ab initio methods. The TBMD basically divides the problem of the dynamical evolution of a system into two, namely: (a) The TB accurate parametrization for the system of interest [9]; and (b) Use of this basis set to calculate the quantum forces to be used in the MD calculation [10]. Since the used basis sets are usually much smaller than in full ab initio calculations, the required matrix diagonalizations are performed much faster.

Therefore, to study the full evolution from a thicker rod, and breaking of a gold nanowire, we have performed TBMD simulations [9, 10]. Details of the procedure we used can be found in Refs. [9–11]. Very briefly, the electronic structure of gold is described using a TB fit developed by Mehl and Papaconstantopoulos [9], which gave very good results when applied to bulk solid and liquid gold, for both static as well as dynamic properties [10]. The electronic structure was calculated using a diagonalization procedure, and the equations of motion along the MD procedure were integrated using the Verlet algorithm with a time step of $\Delta t = 1$ fs. To perform the annealing, we have used a friction parameter $\gamma = 0.001$ fs^{-1}. Brillouin zone sampling was done using the Γ-point. The periodic supercells used in all calculations had dimensions (20 Å, 20 Å, L_W).

In order do supplement our understanding of these thin NWs we have also used first principles DFT [7, 8] methods to the final stages of the evolution and breaking of the wires previously obtained with the TBMD. The reasons for it were two-fold; first ab initio calculations could confirm the TBMD results and, further, they could add information on the electronic structure of the atoms near breaking. Second, using ab initio methods we could study the effect of light impurities and their effect on the structural and mechanical properties of Au NWs. These questions were therefore answered by ab initio total energy DFT calculations for selected structures from the TBMD simulations. Two methods have been used; in some cases we have used a description of the Kohn–Sham orbitals based on a localized basis set, via the SIESTA code [12], which is a fully self-consistent procedure for solving the Kohn–Sham equations [13]. The interaction between the valence electrons and ionic cores are described through standard norm-conserving Troullier–Martins pseudopotentials [14]. Periodic boundary conditions were used with a supercell approximation with lateral separation of 20 Å between wires to make sure that they do not interact with each other. We have used the X-point for the Brillouin zone sampling (tests with 8 Monkhorst–Pack **k**-points [15] along the tube axis were also performed with similar results). After each change in the wire's length, the positions of all the atoms in the supercell were relaxed until all the forces were smaller than 0.03 eV/Å. Calculations were done within the generalized gradient approximation (GGA) [16] for the exchange-correlation functional. Split-valence double-zeta basis set with polarization function, with a confining energy shift of 0.07 eV [17], and a cutoff of 250 Ry for the grid integration [12], were used (a series of tests for both bulk gold and gold dimer gave us confidence that these were appropriate choice). GGA breaking forces for pure Au NWs are in good agreement with the experimental results (1.9 nN, and the experimental result [18] is 1.5 ± 0.3 nN).

Besides the DFT calculations using localized basis set, we have also used a plane waves (PW) basis set to expand the Kohn–Sham orbitals and density. We have employed the VASP code [19], within the GGA approximation [20], with ultrasoft pseudopotentials [21] and a plane wave expansion up to 180 eV. All other approximations were the same as in the SIESTA calculations. These SIESTA and VASP calculations for pure Au NWs provided results that were very similar, and also similar to the previous TBMD results [22]. They served on the other hand to give us more insight into the mechanism of bonding as well as into the electronic structure of these wires [22], and have shown that indeed the breaking distances in pure Au nanowires are not bigger than 3.0–3.1 Å.

Evolution and breaking

TBMD simulations were used to study the evolution of Au wires [11, 22, 23] in an attempt to understand experiments that show atomically thin NWs. As an example, one of such simulations is discussed here. We considered a NW composed of a stack of ten (111) planes of seven atoms each, to study the evolution of gold nanowires under stress. The periodic super-cell had an initial length $L_W = 24.0$ Å along the tube direction. After one thermalization cycle, the initial configuration attained a cylindrical final geometry with the external atoms reconstructing into a densely packed structure. After this thermalization procedure, we repeated cycles where the wire was elongated by 0.5 Å, the temperature was increased to 300 K, and the system was annealed for 4,000 MD steps (4 ps) until a temperature of approximately 30 K was reached. This cycle was repeated until the rupture of the wires. In general terms, the thinning down process is due to a defect structure that leads to the one atom constriction [11, 22, 23]. Once the one atom constriction that separates the two tips is formed, a new process is initiated. Atoms from only one of the tips start to move to the neck, and are incorporated to the one dimensional chain that grows as long as five atoms from apex to apex, with three suspended atoms. The details of the neck formation are presented in Ref. [22].

It is very instructive to follow the structural evolution of the NW if the pulling forces are displayed along with the selected structures. From the total energies of the final configurations of each elongation stage, these forces were obtained. Similarly to recent studies of mechanical properties associated with the formation mechanisms of atomically thin Au nanowires [18], we observe that the dynamical evolution of the nanowires correspond to elastic stages followed by sudden structural relaxations, which are reflected in a sawtooth behavior of the pulling force acting on the wire, as can be seen [22, 23] in Fig. 1 for this simulation.

The simulation presents a feature similar to other ones [22], which is a tendency of the NW to become hollow as it is pulled; this is caused by the motion of atoms from the center of the wire towards its surface, showing that this is a general feature of this type of evolution. As a consequence, the seven-atom planes have a tendency to be transformed into six-atom rings stacked along the tube axis, in the evolution defected parts of the wire start to distort and narrow sections develop. The result is the formation of narrow constrictions that develop into a line of suspended atoms attached to Au atoms from the two leads. From the insets in Fig. 1, it can be seen that the elastic stages
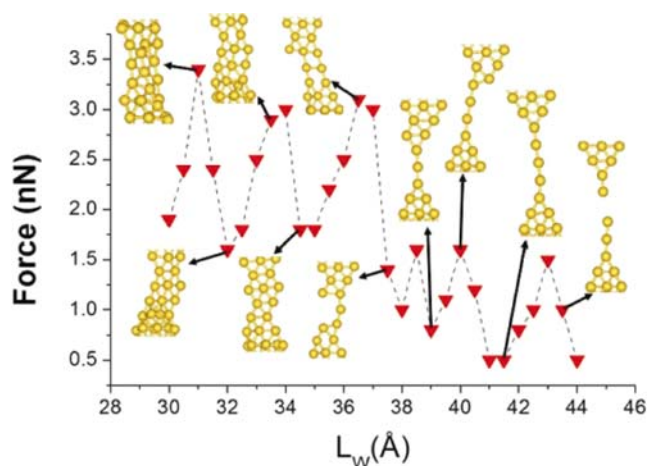
Fig. 1 Calculated pulling force acting on the Au nanowire for selected stages of the simulation. Arrows indicate configurations after major structural rearrangements of the wire

correspond to the building up of stress mostly due to the increase of the interatomic distances. The force relaxations, on the other hand, correspond to either concerted rearrangements of the atoms, mainly at the defective part of the wire (for example the formation of the one atom thick neck occurs mainly in the elongation interval from $L_W = 36.5$ Å to $L_W = 38$ Å), or due to the insertion of a new atom into the chain, after the one atom constriction was formed. After elongation $L_W = 38$ Å, the NW shows the incorporation of other suspended atoms and also displays an one atom wire sideways movement, as the wire grows with incorporation of more atoms. We obtain a value for the applied force right before the breaking of the nanowire around 1.5 nN for this simulation. These results are in good agreement with the experimental value [18] of 1.5 ± 0.3 nN. The final structure in Fig. 1 depicts the wire just after its rupture.

Au NWs obtained using the TBMD gave very nice results and helped the understanding of processes associated with their evolution. Au–Au distances just prior to breaking of the wire, that we refer in short as breaking distances, were all around 3 Å.

Further tests to verify that those were indeed the correct values for the Au–Au breaking distances were done using selected structures from the TBMD calculations. The configurations used had already five neck atoms, but the sizes of the wires were smaller than the TBMD rupture point. The further evolution all the way to breaking was accomplished using ab initio DFT methods. As mentioned above, both SIESTA and VASP codes were used, and no qualitative changes were observed. Breaking distances and breaking forces were all similar within all three methods. This gave us confidence that we had very reliable structures, and

that the presented results were not artifacts of the method used.

Effect of impurities

Au in bulk form is a very stable metal, and this is the main reason for its use as electric contact. The extreme situation presented by these new atomically thin wires deserves investigation, as to what extent impurities would affect the pure NW. Intentional contamination, and more importantly, non-intentional ones, could very well happen inside of even very good vacuum chambers, where some of the experiments are performed.

The research on pure metals NWs have been intense, however, the study of impurities in these systems has increased mostly in the last few years. In fact, from both a fundamental and applied perspectives, it is a natural line of investigation the understanding of how other atomic and molecular species affect the mechanical, structural and electrical properties of these NWs. This line of research may be viewed as "nanocatalysis". In this context, research has focus on gold nanostructures [24–26], that have been found experimentally, as well as theoretically, to exhibit catalytic properties.

Investigations of the behavior of NWs contaminated by atomic and molecular species have appeared in the literature. Some examples are the studies of metal NWs in solution [27, 28], and the theoretical investigation of the effect of small molecules, such as thiol [29], or atomic species, such as hydrogen, carbon, oxygen, and sulfur [30], focusing in the possibility that such impurities could be responsible for the experimentally observed, in HRTEM [31] measurements, large Au–Au distances of ≅3.6 Å. These works have focused in the fact that HRTEM experiments do not show the presence of possible contaminant light impurities. Attempts to answer this question using intentional doping with selected species have been also pursued [32, 33].

We have been studying the interaction of light impurities and small molecules with Au nanowires, and we have focused on how these impurities may alter the mechanical properties of these NWs. In fact, it is an interesting result that a single atom, for example, oxygen, when inserted in the NW neck can produce a drastic effect on the properties of the pure system. In order to study this problem, we have performed first principles calculations using the two basis set expansions mentioned previously for pure nanowires. The first calculations with impurities were performed by bringing the impurity nearby the one atom

chain. We observed that the impurity was, eventually, incorporated into the one atom chain. Due to this result, in all further studies with impurities we have included them directly along the chain line [30]. Therefore, contaminated structures were generated for the nanowires in the following way: Starting from an ab initio configuration for the pure NW prior to the rupture, as discussed above, we inserted the desired impurity in the neck, after which all the atoms were allowed to relax. After insertion of the impurity and relaxation of forces, the obtained structure was pulled until rupture, similarly to the pure case discussed in the last section. In all cases studied, the wire never broke in the Au–X bond (X represents an impurity). This seems to be a general property of all the single impurities that we have investigated. See Ref. [30] for more details. Many different impurities [30, 34] were studied; C, H, O, N, B, and S, and some small molecules; CH, CH_2 and H_2. We discuss some of them here.

Hydrogen is an impurity that even under ultra high vacuum conditions might be present and, therefore, could be incorporated into the NW. H is therefore a possible candidate to be found in Au nanowires. Using VASP we have investigated a variety of structures with different number of H atoms inserted in the neck of the NW, as shown in Fig. 2. We first considered contamination by one single H in the NW. In Fig. 2a we depict the structure prior to the rupture, and in Fig. 2b after the breaking. The relevant interatomic distances are presented in Table 1. As can be seen, the Au–H–Au distance prior to breaking has a value of approximately 3.6 Å (a similar result was also obtained [30] using the SIESTA code, as shown in Table 1). This is a strong indication that unless the experimental set up will disrupt the structure of the NW, it seems that H would
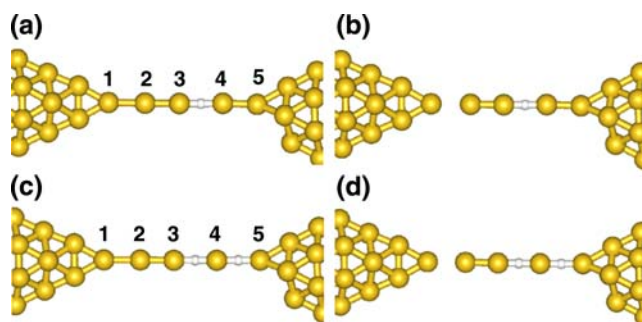
Fig. 2 Final stages of evolution of Au nanowires with different numbers of inserted H impurities (using VASP code). Numbers label the atoms that are in the neck and bond distances are given in Table 1. (**a**) and (**b**) show the wire with only one H atom just before and after the rupture, respectively. (**c**) and (**d**) show similar configurations for two H atoms

Table 1 Bond distances (i,j) (in Å) between the atoms Au_i and Au_j in the neck of the structures with inserted H impurities shown in Fig. 2a and c

NW	(1,2)	(2,3)	(3,4)	(4,5)	F (nN)
a	**3.04**	2.84	3.6	2.84	1.71
Ref. [30]	**3.06**	2.82	3.62	2.87	1.7
c	**3.05**	2.81	3.58	3.62	1.58

Breaking forces are also presented. The bold face distances mark the bond where the wires break. We show, for comparison, the results [30] for calculations with one H impurity obtained using the SIESTA code

be the most likely impurity responsible for the measured Au–Au distances in the range of 3.5–3.6 Å.

To further argue our case, we proceeded to include more H atoms in the NW's neck. In Fig. 2c and d, we present configurations for the Au NW just before and just after the breaking, respectively, with two inserted H atoms in neighboring Au–Au bonds. When two H atoms contaminate the NW with an arrangement Au–H–Au–H–Au, we obtain two similar distances of 3.6 Å, in reasonable agreement with experimental results of Ref. 31.

So far there are still no experiments that can directly probe the nanowires to answer the question which, if any, impurities are causing the large Au–Au distances. Attempts of intentional doping may help, but indirect information provided by another type of experiment recently performed have shed some light into this problem. Zahai et al. [35] have performed experiments with Au clusters obtained from bulk Au. These experiments have shown that the only clusters that incorporate H are Au dimers. Furthermore, they have shown that a linear structure Au–H–Au is stable, and gives an Au–Au distance of 3.44 Å, which compares rather well with our results for H in Au nanowires if we consider the different environments, and the fact that the dimer is not under stress. If such dimers, as those produced by Zahai et al. were part of a nanowire under tension, it is reasonable to imagine that they would give the observed experimental values around 3.6 Å. We believe that these experiments point to H as a possible contaminant in Au nanowires, and very likely the one responsible for the large Au–Au distances. As a final point, we have also calculated the maximum pulling forces for the H-contaminated wires, and they are in the range of 1.6–1.7 nN [34].

Carbon is also a possible contaminant, and probably for this reason, it was considered as a likely candidate to explain the large Au–Au distances [36]. In order to check if that could be the case, we have studied C in many different configurations in the NW neck; we considered structures with five and four Au atoms in

the neck, and for this latter geometry, the C was taken either in a symmetrical or an asymmetrical position. As in the case of H, the initial relaxed geometries of the wires were quasi-statically pulled all the way up to their rupture. In all cases, the behavior of C as a contaminant was to make the Au–C–Au bond of the order of 3.85–3.9 Å [34], values that are larger than the experimentally reported values of 3.5–3.6 Å. The Au–C distances remain almost constant during the stretch of the wires, with values close to 1.9 Å. Here we show one example of such calculations using VASP. Figure 3a shows a gold nanowire with a C atom inserted between the Au atoms labeled 1 and 2, therefore, in an asymmetric position in the NW. The Au–C–Au is a very stiff bond that results in an Au–C–Au distance of 3.85 Å, with the breaking occurring at the 3–4 bond, as shown in Fig. 3b. The Au–Au bond that breaks attains a maximum interatomic distance of 3.05 Å, and the pulling force prior to rupture is 1.36 nN. Both these values are similar to what is obtained for pure NWs, which is what should be, since the rupture occurs in a pure Au–Au bond in both cases.
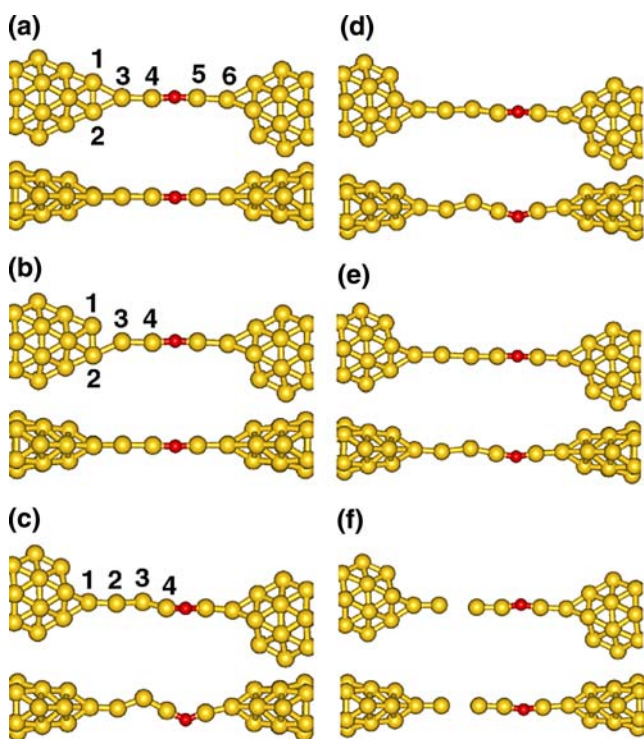
For the same reason as carbon, oxygen was one of the impurities that we have investigated (using SIESTA), in order to see if it could be responsible for the large Au–X–Au distances. As it turned out, the Au–O–Au distance too was too large, and therefore O would not be the contaminant responsible for the observed Au–X–Au around 3.6 Å. Nevertheless, it turned out to be a very interesting system. Oxygen that is not reac-
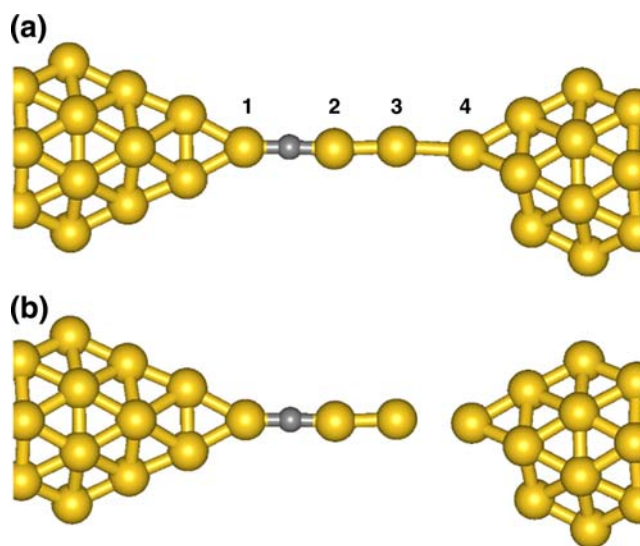
Fig. 3 Final stages of evolution of Au NW with C impurity using the VASP code. Numbers refer to the Au atoms in the neck and bond distances and angles are given in the text. (**a**) is the structure with C, just prior to rupture, whereas (**b**) is the same NW after the breaking

tive to Au even in Au surfaces, can become significantly more reactive when gold forms small clusters, or nanowires under tension [37]. Here we considered the effect of the contamination of one O atom to an Au NW with 4 atoms in the neck. The final stages of the evolution of the NW with one O impurity are displayed in Fig. 4, for a sequence of configurations of the wire all the way up to its rupture.

One property of oxygen that puts it apart from all other impurities studied, is the fact that metal atoms were extracted from the tip, as shown in Fig. 4a through Fig. 4c. Figure 4a displays the nanowire after O contamination in a symmetrical configuration, in the middle of the four Au neck atoms. Figure 4b shows the bond Au_1–Au_3 starting to break, and in Fig. 4c, after tip rearrangements, the Au_2 atom is also extracted from the tip, and atom Au_1 becomes the first neck atom. This neck-tip reconstruction releases the stress in the NW, and is characterized by a sudden drop in the pulling force, as shown in Table 2. We observe that after this stress release, as the neck becomes larger, it forms a zig-zag structure with angles Au_2–Au_3–Au_4 of 129° and Au–O–Au of 135°, as can be seen in the second view of Fig. 4c. As the wire is pulled, these angles open up, and in Fig. 4d they are 162° and 162°,

Table 2 Bond distances (i,j) (in Å) between the atoms Au_i and Au_j in the neck of the structures with inserted O impurities shown in Fig. 4

NW	(1,2)	(1,3)	(2,3)	(3,4)	(4,5)	(5,6)	F (nN)
a	2.71	3.06	2.97	2.82	4.20	2.82	2.1
b	2.71	3.17	2.99	2.84	4.21	2.84	2.3
c	2.65	–	2.66	2.59	3.70	2.61	0.4
d	2.71	–	2.73	2.63	3.89	2.66	1.1
e	2.79	–	**2.98**	2.69	4.07	2.73	1.7

Breaking forces are also presented. The bold face distance marks the bond where the wire will break

respectively. This straightening of the structure continues until the breaking of the wire. Once again, the rupture occurs at an Au–Au bond with the force around 1.7 nN, a result within the experimental value of 1.5 ± 0.3 nN, which is expected since for a pure Au–Au bond breaking.

Au tips have a rather stable configuration, as already discussed [11]. In fact, all the other systems that we have studied so far simply evolved in such a way that one of the Au–Au bonds in the neck broke. But the structure of the tips was never modified. From these results, we conclude that oxygen is in some sense a special type of impurity, since it stabilizes the neck in such a way that upon application of stress the system favors the removal of atoms from the tip, rather than rupturing. This occurs because the oxygen allows the neck to withstand larger forces when compared to the pure nanowire, of the order of 2.3 nN, as shown in Table 2. Therefore, what the oxygen is most likely doing is affecting the local electronic structure of the neck via strong covalent-like bonds, besides the metallic bond character already present in the pure Au wires. This prediction was made recently [38] with a suggestion that judicious contamination with O could help the development of longer one atom chains. Experiments using intentional oxygen doping have been performed, with results along the lines of our proposal [39].

A recent calculation [40] of organic molecules attached to an Au surface, have also observed a behavior similar to the case of the O impurity. That simulation showed that, when the molecular structure is pulled out of the surface, instead of breaking somewhere along its structure it became a composite system, namely, a molecule attached to an Au nanowire, which was extracted out of the Au surface. Similarly to the oxygen-doped nanowires simulated in the present work, the molecule instead of breaking when pulled out from the surface, draws out with it an one atom thick NW with a few atoms, that upon stretching will eventually break.

Fig. 4 Final stages, (from (**a**) to (**f**)), of the evolution of an Au nanowire with an O impurity up to its rupture (two views of each elongation are displayed). Numbers refer to the atoms that are involved in major rearrangements in the nanowire's neck and tip

Conclusions

In this paper, we discussed some aspects of the physics of metal NWs. We showed that the use of a few simulation methods (TBMD, ab initio DFT—SIESTA, VASP) all based in the DFT, can help the understanding of many questions presented by experiments. Moreover, we have also showed that such tools can have predictive power, as the final example of the possible use of O impurities to produce longer atomic Au chains. The results of evolution of Au NWs obtained with the use of TBMD used in conjunction with ab initio calculations have shown that TBMD structures are very reliable, since the conclusions from all these calculations were very similar. In particular, the result that breaking distances for pure Au NWs are around 3.0–3.1 Å, this result being independent of the simulation method.

With the aim of explaining the large experimentally observed Au–Au bonds distances of ~3.6 Å, we have studied the effect of contamination of these NWs with light impurities. In the process of studying these contaminants, we have obtained very interesting results. As to the explanation of the large observed Au–Au bonds, the only impurity among all studied one that gave results similar to experiments were H impurities, and we believe, if the rupture happens in the quasi-static limit, that it is most likely the one responsible for the observed distances. Carbon was discarded since it gave too large distances in this especial environment of Au NW under stress. Oxygen, which as a candidate for the large distances could not explain the experimental results, gave instead a possibility of its use as extractor of Au atoms. Therefore, we have predicted [38] that it could be used as a tool to make longer Au atomic chain NWs. Experimental results along these lines have been produced [39]. This research leaves a lot of questions still unanswered. For example, if carbon atoms are really present in the ambient of formation of these NWs why Au–Au distances of the order of 3.9 Å, which are the largest Au–C–Au distances that we have obtained in our simulations, have not been experimentally observed. Either C atoms cannot be incorporated in the necks, or other effects, like the e-beam in the HRTEM experiments, are influencing the rupture of these NWs. We intend to investigate these issues. Also, another relevant topic, that may even help to identify the character of these impurities, will be the understanding of their effect on the charge transport across these NWs. Some other important questions are how to control the insertion of these impurities, and also, how to make use of their novel properties in the design of new devices. We hope that the results presented here stimulate more theoretical, as well as experimental work in this interesting field of metallic NWs.

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